GEOCHEMISTRY

Project title: Oxygen Isotope Geochemistry and U-Pb Dating of Zircons of Yellowstone Volcanic Rocks

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Additional investigator(s): John Valley

Objective: To 1) understand the generation of oxygen-18 depleted rhyolites inside of Yellowstone caldera; 2) estimate zircon crystallization and residence time in silicic magma chambers; and 3) date volcanic units using U-Pb analyses of zircon with an ion microprobe.

Findings: Oxygen-18 depleted rhyolites were produced as a result of total remelting of hydrothermally altered rocks in the downdropped caldera block. Two papers are written (Bindeman and Valley, "Formation of low-delta-18-O rhyolites after caldera collapse at Yellowstone," *Geology* 28, n8, p. 719-722.; and Bindeman and Valley (2000) "Low-delta-18-O rhyolites from Yellowstone: Magmatic evolution based on analyses of zircons and individual phenocrysts." *J of Petrology,* August 2001). Dating of zircons with an ion microprobe revealed that the majority of zircons in post-Lava Creek tuff, and post-Huckleberry Ridge tuff intracaldera lavas is inherited from the older Yellowstone rhyolites. A paper (Bindeman, Valley, Wooden, Persing (2001) "Post-caldera volcanism: In situ measurement of U-Pb age and oxygen isotope ratio in Pleistocene zircons from Yellowstone caldera," *Earth and Planetary Science Letters,*) is accepted for publcation. U-Pb zircon ages of Lava Creek Tuff and Huckleberry Ridge Tuffs are similar to Ar/Ar ages.

Project title: Investigation of CO2 Emissions Related to the Yellowstone Volcanic/Hydrothermal System

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Objective: To 1) estimate the CO_2 emissions from the Yellowstone volcanic/hydrothermal system; 2) monitor background temporal variability of CO_2 emissions, and how variations are related to changes in hydothermal and seismic activity; 3) study the spatial distribution of CO_2 emissions and investigate controls on spatial heterogeneity of gas emissions; and 4) monitor gas chemistry including carbon and helium isotopes to gain a broader understanding of the sources of gas emissions and interactions with the hydrothermal system.

Findings: A stratified-adaptive sampling plan was designed to estimate CO_2 degassing in Yellowstone National Park, and applied in the Mud Volcano thermal area. The stratified component focused effort in regions with the most spatial heterogeneity (high-flux regions). The maximum and minimum measurements for vent and diffuse fluxes were 1.7×10^8 and 6.3×10^4 mols/yr, and 32,000 and 4.0 g/m2day, respectively. Fluxes observed in most vegetated regions of Mud Volcano were similar to values reported by agricultural studies (less than 38 g CO_2/m2day). However, we also found a few high-flux vegetated sites (up to 5,000 g/m2day) that are likely thermal features that have waned in thermal activity, yet are preferred pathways for degassing of deep CO_2. Vent degassing (0.76 to 2.5×10^9 mols/yr) accounts for 32 to 63 percent of the total degassing observed at Mud Volcano (2.4 to 4×10^9 mols/yr). Temporal variation of CO_2 emissions was observed to correlate with soil moisture, and environmental conditions. Results were published in Werner, et al, 2000, "CO_2 Emissions related to the Yellowstone Volcanic System: 2: Statistical Sampling, Total Degassing, and Transport Mechanisms," *Journal of Geophysical Research,* Vol.105, B5, 10,831-10,846 and Boomer, K., Werner C., and Brantley, S.L., 2000, "CO_2 Emissions related to the Yellowstone Volcanic System: 1: Development of a Stratified Adaptive Cluster Sampling Plan," *Journal of Geophysical Research,* 105, B5, 10,817 -10,830.

Surface degassing measurements in the Obsidian Pool region of Mud Volcano were used to test eddy correlation (a micrometeorological technique) as a means to measure volcanic and geothermal emissions. Results of this preliminary investigation suggest that eddy correlation is a viable alternative to typically used chamber methods used to measure degassing in geothermal areas. Results were published in Werner et al., 2000, "Eddy-Correlation Measurement of Hydrothermal Gases," *Geophysical Research Letters,* Vol. 27, No. 18 , 2925-2929.

Preliminary investigation of the CO_2 emissions in Upper Geyser Basin; Mammoth Springs; Roaring Mountain; Washburn Springs; Crater Hills; and the Lamar River Valley suggest that diffuse degassing is highest in acid-sulfate and travertine precipitating regions, and lowest in regions of silica precipitation and sulfur flows. Further degassing measurements are planned for summer 2001. We are currently estimating the CO_2 emissions for the Yellowstone system using geologic and geochemical constraints.

Project title: Water Chemistry and its Relationship to Local Geology: A Yellowstone Case Study

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Objective: This study is an ongoing component of Geology 329 taught from the Indiana University

Geologic Field Station, Cardwell, MT. During the course of the field-based class, undergraduate students involved with several environmentally oriented programs on campus are involved in their first major field experience. The objectives of this study are two-fold. First, the Yellowstone field trip provides a unique opportunity to look at an ecosystem that is heavily influenced by hydrothermal activity, which is in stark contrast to the riparian and montane systems in the course study areas of the Tobacco Root Mountains. During the weeks preceding the Yellowstone trip, the students engage in the collection of field measurements of various aquatic systems encountered in their study areas. This data set (including oxidation-reduction potential, pH, temperature, and specific conductance), us used as a comparative set against the data collected in the thermal features of Yellowstone.

Findings: The findings of the 2000 field season indicate that within the Norris Geyser basin, there have been remarkable shifts in the heat centers during the last 40 years. There are several springs that are no longer active at the surface, and new springs have developed. The centers of highest recorded temperatures have shifted within the basin and are typically to the west of the major 1960s centers of highest temperatures. Again, this was an excellent illustration of the ephemeral nature of these features.

The visit to the backcountry spring from the Firehole Lake Drive was an excellent illustration of the influence of temperature on the other parameters of aqueous geochemistry. Careful measurements of the oxidation-reduction potential, pH, and specific conductance were analyzed and the values plotted with distance from the main pool. The chemical parameters recorded were well matched to the physical features observed (microbial community color, precipitation of mineral phases, and adjacent vegetation).

The overall Yellowstone experience of the course participants was one of the most highly rated portions of the course. Within a very concentrated area, students were able to observe and apply principles of aqueous geochemistry and in turn observe the influence the waters have on the communities of plants and animals around them. We hope to extend the research permit to continue the development of the course database for the students work with.

Project title: Geochemistry and Geochronology of Eocene Potassic Volcanism in the Absaroka Volcanic Field

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Additional investigator(s): Charles Lindsay

Objective: Our objective is to carry out a geological and geochemical transect across the northern part of the Eocene Absaroka volcanic field. Because the Absaroka volcanic rocks record one of the most voluminous and compositionally diverse magmatic episodes to affect the Cordillera during the Eocene, the results obtained from this study will improve our knowledge of the ages, compositions, and petrogenesis of Tertiary magmatism in the northern Rocky Mountains. This, in turn, will provide insight into the fundamental problem of how rock suites with arc-like geochemical features can form in such different tectonic environments and possibly in the absence of contemporaneous subduction. The targeted areas in Yellowstone National Park are the Mt. Washburn-Observation Peak volcanic center, the Sepulcher Mountain-Electric Peak eruptive center, and the Sylvan Pass-Eagle Peak eruptive center.

Findings: Our work in the Absaroka volcanic rocks during the previous year is summarized as follows: Whole-rock major and trace element abundances were determined for 40 stratigraphically constrained lava flows from Sepulcher Mountain (SM) and 17 hypabyssal intrusive units at adjacent Electric Peak (EP). SM lavas are predominately augite +/- enstatite basaltic-andesites, hornblende andesites, and hornblende +/- biotite dacites. EP intrusive units include biotite +/- hornblende quartz diorites, tonalites, and granodiorites. Petrographically, both intrusive and extrusive samples exhibit strong evidence of mixing and/or assimilation (mafic inclusions, resorbed cellular plagioclase, heterogeneous glass/groundmass compositions, and partially resorbed xenoliths). Rocks from SM and EP are compositionally similar and define a high-K, calc-alkaline series with compositions ranging continuously from 55-73 wt percent SiO2, 1.9-4.0 wt percent K2O, and Mgno. from 56-27. Major-element variation diagrams define roughly linear arrays, while the compatible trace elements Ni and Cr define both mixing and fractionation trends. Trace element abundances are characterized by extreme LILE (Ba, Rb, K) enrichment (100-400 X chondrite, ~2000 ppm Ba) and HFSE (Nb, Ta, Zr, Hf) depletion (3-50 X chondrite). Chondrite-normalized REE patterns are broadly similar for all rock types, characterized by concave-up fanning patterns, strong LREE enrichments (Ce/Yb n = 10-36), and no Eu anomalies. Some evolved magmas have lower REE abundances than mafic magmas. The large range in incompatible trace element ratios (Hf/Ta = 7-12 for the least evolved magmas and K/Rb = 275-575 for the entire suite) are consistent with REE abundances and suggest that the suite cannot be related to a single parental magma by simple fractionation processes. Based on these data, we hypothesize that the calc-alkaline signature results from mixing with and assimilation of crustal melts (coupled with fractional crystallization) by multiple parental compositions. The calc-alkaline nature of the magmas appears to be inherited from interaction with continental crust.

Project title: Biogeochemistry of Hydrothermal Springs

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Objective: 1) Investigate geochemical variations in microbial mats, pore waters, siliceous sinters and geyserites at different hot springs and thermal drainages in the park. Results will be compared with stages of silica diagenesis and geochemistry; 2) Investigate the local hydrogeological characteristics of hot spring-influenced drainages. Results will be used to calculate mass balances for such drainages, to determine silica deposition rates in sinter mounds and to determine interaction with local groundwater; 3) Investigate photochemical processes in thermal springs of various composition.

Findings: During the past year, work focused on expanding research activities in the area of hydrogen peroxide cycling. The topic has become far more significant than previously realized. Originally of significance as an environmental factor, it is now clear that the presence of reactive oxygen species, of which hydrogen peroxide is one, is significant in determining internal and external responses of organisms to stress. Specifically, it has implications for enzyme evolution and for cellular function and repair. Implications for the conversion of solar energy to chemical energy are of equal importance. All of these topics are relevant to efforts to assist in the design of better tests for life on other planets as well as in understanding the origin of life on our own planet.

Much of the effort on the geochemistry of hydrothermal springs in 2000 focused on hydrogen peroxide production. Hydrogen peroxide production and cycling was essentially absent in all thermal springs examined likely as a consequence of fire-induced haze. The haze filtered nearly all of the UV radiation, reducing photochemical reactions to extremely low rates. The decay rates, as measured on field samples, were higher than values previously measured. As a consequence, hydrogen peroxide concentrations were not observed at detectable levels. Other biogeochemical cycles were also suppressed; iron and sulfur cycling was not observed.

Project title: Arsenic Biogeochemisry in Yellowstone National Park

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Objective: Our work will focus on geochemical and microbiological processes that influence the speciation and behavior of arsenic in thermal environments. Given the toxicity and potential negative impacts that arsenic (As) may have on biota in non-park environments, the thermal springs represent a potentially informative model system to begin to understand how microbiological life forms metabolize or detoxify As.

Findings: We obtained data on the oxidation of arsenite to arsenate in several hot springs in the Norris Geyser Basin. A detailed study was conducted in one acidic spring where rates of arsenite oxidation were determined along with a suite of other aqueous and sediment characteristics. Arsenate oxidation seems to be linked to the disappearance of sulfide from the spring water and to the presence of certain thermophilic microbial species.

Project title: Sulfur Speciation and Redox Processes in Mineral Springs and their Drainages

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Objective: The primary objective is to determine the actual speciation of dissolved sulfur species as they undergo oxidation and volatile losses of H2S. Intermediate sulfoxyanions such as thiosulfate have been implicated as complexing agents to solubilize and mobilize metals in the formation of ore deposits and as monitors of volcanic activity. We hope to relate sulfur speciation in hot springs and their overflow drainages to rates of oxygen diffusion and solubility.

Findings: We have found thiosulfate in many hot springs throughout the park and we find it primarily formed from the oxidation of H2S. In a few rare cases the concentration of thiosulfate on a molar basis (or weight basis) is present in higher concentration than H2S. For these springs, thiosulfate is the main form of reduced sulfur dissolved in the water. These data and their interpretations can be found in 2 USGS open-file reports and in 2 scientific publications listed in the bibliography. One pool in particular, Cinder Pool, not only has high thiosulfate but is the only place where polythionate has been found. In this pool thiosulfate is likely to be forming from hydrolysis of a molten sulfur layer known to exist at 18-20 meters depth. The polythionate has been shown to be formed from thiosulfate and catalyzed by pyrite that occurs within the floating cinders on the pool's surface. One scientific paper is devoted to a description of the complex chemistry of sulfur at Cinder Pool. Any evidence for thiosulfate to be important in the formation of hydrothermal ore deposits is largely discredited.

Project title: Honors Freshman Quantitative Analysis

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Objective: To give honors freshman chemistry students (CHM 1215) a real-world example of a total alkalinity titration.

Findings: Total alkalinity titrations were performed as described in Harris's Quantitative Chemical Analysis, but the many months intervening between collection and analysis rendered the results useful only as an exercise.

Project title: Field Trip to Yellowstone National Park, Water Sampling

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Objective: Investigation of water composition at a variety of park locations in an effort to correlate the original fate and history of the solutions.

Findings: Several years of collection trips have identified a variety of geothermal surface features including neutral chloride, acid sulfate, and alkaline carbonate. Additionally, surface waters in the Sheepeater Cliff area have to some degree been linked top the spring waters at Mammoth Hot Springs. Surface waters near Madison Junction were thought at one time by our researchers to be contaminated with municipal waste treatment contaminants, but this past year we determined that excessive chloride detections were from natural sources.

Project title: Geochemical and Geophysical Investigations of Mine Impacts and Watersheds, Yellowstone National Park

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Objective: The fundamental goals of this project are to contribute to the understanding of the complex geochemistry of the Soda Butte Creek watershed, and to investigate the impact of mining activities near the creek's headwaters. This is accomplished through: 1) building a long-term database documenting seasonal variations in stream chemistry and metal concentrations in stream waters and sediments, and 2) delineation of shallow subsurface features in the Soda Butte Creek floodplain.

Findings: Elevated concentrations of metals (Cu, Zn, Fe, Ag) are recorded in sediments immediately downstream of the McLaren mine tailings. Concentrations decrease sharply with distance from the tailings, and generally return to background levels within four miles downstream. Although the mine tailings are a significant source of contaminants, Republic Creek also contributes substantial amounts of nickel and related metals; nickel concentrations remain elevated throughout the length of Soda Butte Creek to the Lamar confluence. Hydrothermal tributaries at Soda Butte Mound and Warm Creek influence stream chemistry, at times contributing significant dissolved species. Seasonal variations in contaminants are evident. Low flow conditions generally favor higher concentrations in sediments, while high flow conditions tend to dilute concentrations and distribute contaminants a greater distance downstream from the source. This study will continue with field measurements and sampling of stream sediment and waters on a seasonal basis.

Project title: Geology and Geochemistry of Thermal Springs in YNP

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Objective: To teach students the interrelationship between the geological setting and geochemistry of thermal springs.

Findings: The Department of Geology at the University of Georgia conducted an eight week summer field course in geology and anthropology in 1999. As part of this course, a group of 24 students, this instructor, and 3 teaching assistants visited various thermal areas within YNP on July 30, 2000.